

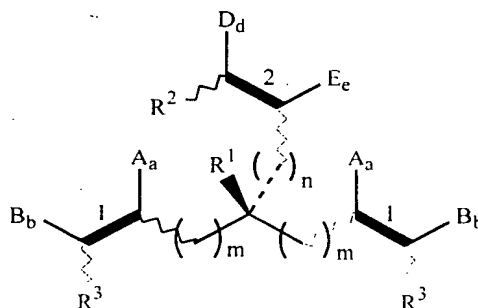
16 JUN 2001 CLAIMS

1. A method for desymmetrization, comprising:
providing a molecular substrate having a plane of symmetry; and
5 causing an olefin metathesis reaction involving the molecular substrate to occur to
form a product free of a plane of symmetry.
2. A method as in claim 1, wherein the desymmetrization is a catalytic desymmetrization
and the providing step further comprises providing a catalyst.
- 10 3. A method as in claim 1, wherein the molecular substrate is selected from the group
consisting of achiral and meso substrates.
4. A method as in claim 1, wherein the molecular substrate is selected from the group
15 consisting of cyclic and acyclic substrates.
5. A method as in claim 1, wherein the product is selected from the group consisting of
cyclic and acyclic products.
- 20 6. A method as in claim 1, wherein the product includes at least one ring having a ring
size of less than about 20 atoms.
7. A method as in claim 1, wherein the product includes at least one ring having a ring
size of less than about 10 atoms.
- 25 8. A method as in claim 2, wherein the catalyst is present in an amount of less than about
15 mol%, relative to an amount of substrate.
9. A method as in claim 8, wherein the catalyst is present in an amount of less than about
30 10 mol%.
10. A method as in claim 8, wherein the catalyst is present in an amount of less than about

5 mol%.

11. A method as in claim 8, wherein the catalyst is present in an amount of less than about 1 mol%.

12. A method as in claim 1, wherein the molecular substrate comprises a structure:



wherein "1" and "2" can be the same or different and each of "1" and "2" denotes a bond selected from the group consisting of a double bond and a triple bond; a, b, d, and e can be the same or different and each of a, b, d and e is an integer equaling 0 to 1; m and n can be the same or different and each of m and n are integers equaling 0-20; A, B, D, E and R¹ - R³ can be the same or different and each of A, B, D, E and R¹ - R³ is selected from the group consisting of hydrogen, hydroxy, C₁-C₂₀ alkyl, C₁-C₂₀ alkenyl, C₁-C₂₀ aryl and C₁-C₂₀ alkynyl, wherein C₁-C₂₀ alkyl, C₁-C₂₀ alkenyl, C₁-C₂₀ aryl and C₁-C₂₀ alkynyl are hydrocarbons optionally interrupted by a functional group including at least one non-carbon element.

13. A method as in claim 12, wherein each of m and n are integers equaling 0-10.

20 14. A method as in claim 12, wherein the functional group including at least one non-carbon element is selected from the group consisting of O, S, Se, silane, silyl ether, carbonyl, carboxyl, carboxylate, ether, ester, anhydride, acyl, cyano, NO₂, alkyloxy, aryloxy, hydroxy, hydroxyalkyl, amino, alkylamino, arylamino, amido, thioalkyl, thioaryl, sulfonate, phosphate, phosphonate, phosphane and stannane.

15. A method as in claim 1, wherein the molecular substrate comprises a structure:

least 80 % optical purity, M is a transition metal ion, and R¹ and R² can be the same or different, and each is selected from the group consisting of C₁-C₁₂ alkyl, heteroalkyl, aryl, heteroaryl and adamantyl.

5 60. A method as in claim 59, wherein R¹ is selected from the group consisting of 2,6-dimethylphenyl, 2,6-diethylphenyl and 2,6-diisopropylphenyl and R² is selected from the group consisting of methyl, ethyl and phenyl.

61. A method for desymmetrization, comprising:
10 providing a molecular substrate having a plane of symmetry; and
allowing a desymmetrization reaction to occur in the absence of solvent to form a product free of a plane of symmetry.

62. A method as in claim 61, wherein the desymmetrization is a catalytic
15 desymmetrization and the providing step further comprises providing a catalyst.

63. A method as in claim 61, wherein the desymmetrization reaction is a carbon-carbon bond forming reaction.

20 64. A method as in claim 63, wherein the desymmetrization reaction is an olefin metathesis reaction.

65. A method as in claim 64, wherein the olefin metathesis reaction is selected from the group consisting of a ring-closing and a ring-opening reaction.

25 66. A method as in claim 64, wherein the molecular substrate is a first molecular substrate, the method further comprising a second molecular substrate and the olefin metathesis reaction is a cross-metathesis reaction.

30 67. A method as in claim 62, wherein the desymmetrization reaction causes at least one enantiomer of a product to form in an enantiomeric excess of at least about 20% at a turnover number of at least about 5.

68. A method as in claim 67, wherein the at least one enantiomer is formed in an enantiomeric excess of at least about 50%.

69. A method as in claim 67, wherein the at least one enantiomer is formed in an enantiomeric excess of at least about 85%.

70. A method as in claim 67, wherein the at least one enantiomer is formed in an enantiomeric excess of at least about 90%.

71. A method as in claim 67, wherein the at least one enantiomer is formed in an enantiomeric excess of at least about 95%.

72. A method as in claim 67, wherein the at least one enantiomer is formed in an enantiomeric excess of at least about 99%.

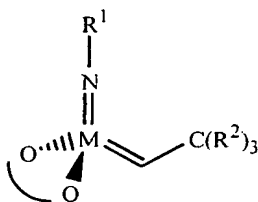
73. A method as in claim 67, wherein two enantiomers are formed in an enantiomeric excess of at least about 20%.

74. A method for catalytic desymmetrization, comprising:
providing a molecular substrate having a plane of symmetry and a catalyst; and
allowing a desymmetrization reaction to occur to form a product having a quaternary carbon center in at least about 20% enantiomeric excess.

75. A method as in claim 74, wherein the desymmetrization reaction is a carbon-carbon bond forming reaction.

76. A method as in claim 75, wherein the desymmetrization reaction is an olefin metathesis reaction.

77. A composition comprising a structure:



wherein M is a metal ion and $\begin{pmatrix} \text{O} \\ \text{O} \end{pmatrix}$ is a chiral dialkoxide of at least 80 % optical purity, the

dialkoxide having sufficient rigidity such that a $\text{M}=\text{C}(\text{R}^2)_3$ reaction site is of sufficient

5 shape specificity, defined in part by the dialkoxide and a $\text{M}=\text{N}-\text{R}$ site, to cause a molecular substrate having a plane of symmetry to react with a $\text{M}=\text{C}$ center at the $\text{M}=\text{C}(\text{R}^2)_3$

reaction site, forming a catalytic olefin metathesis product that has at least a 50 % enantiomeric excess of at least one enantiomer present in the mixture, the product being free of a plane of symmetry.

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78. A method for performing a kinetic resolution, comprising:
 providing at least one substrate having at least one olefin group;
 selecting a catalyst of sufficient steric bulk to initiate an olefin metathesis reaction
 involving the at least one substrate to achieve a k_{rel} of at least about 10.

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79. A method as in claim 78, wherein the reaction is selected from the group consisting of a ring-opening metathesis reaction, a cross-metathesis reaction and a ring-closing metathesis reaction.

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80. A method for performing an asymmetric olefin metathesis reaction, comprising:
 providing a substrate comprising at least one olefin group associated with a ring structure;
 reacting a catalyst with the substrate to initiate an olefin metathesis reaction to achieve a k_{rel} of at least about 5.

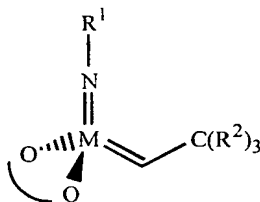
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81. A method as in claim 80, wherein the reaction further comprises a kinetic resolution.

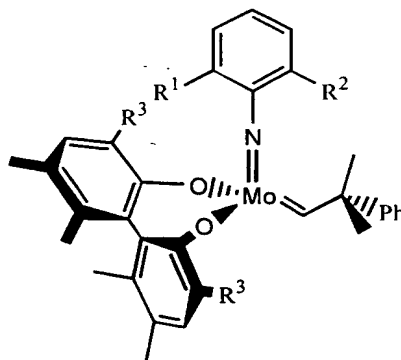
82. A method for performing an asymmetric olefin metathesis reaction, comprising:
 providing two substrates, each substrate containing at least one olefin group;
 reacting a catalyst with the substrates to form a product having an enantiomeric excess
 of at least about 50%.

83. A method as in claim 82, wherein the reaction is selected from the group consisting of
 a ring-opening metathesis reaction, a cross-metathesis reaction, kinetic resolution and a
 combination thereof.

84. A method as in any one of claims 78, 80 or 82 wherein the catalyst comprises a
 structure:



85. A method as in claim 84, wherein the catalyst comprises a structure:



wherein $R^1 - R^3$ can be the same or different and each is selected from the group
 consisting of hydrogen, alkyls, aryls, alkaryl and substituted derivatives thereof.

86. A method as in claim 85, wherein R^3 is selected from the group consisting of ethyl, *i*-
 Pr, *t*-Bu and adamantyl and R^1 and R^2 selected from the group consisting of *i*-Pr and methyl.

87. A method as in claim 85, wherein R^1 is CF_3 and R^2 is hydrogen.